COATINGS AND ENAMELS

UDC 666.597:666.293.521

STRENGTH OF ADHESION OF PRIMER COAT WITH ADDITIVES TO NICKEL-CHROMIUM ALLOY IN MAKING CERMET DENTAL CROWN

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Translated from Steklo i Keramika, No. 6, pp. 23 – 25, June, 2006.

The effect of tin oxide and calcium phosphate on the strength of adhesion of material for an artificial tooth primer coat to the metallic crown is considered. An alternative method for fast determination of the strength of adhesion of metal to ceramics using a Micro Scratch Tester instrument is based on depositing a scratch on a finished coating with a diamond indenter. It is found that the hydroxyapatite additive ensures the optimum adhesion.

One of the main characteristics that are significant for adequate service of cermet dental prostheses is the strength of the ceramic layer and its adhesion to metal. The strength of adhesion of the metal and ceramic layers depends on several factors: coordination of the CLTE of the coating and the substrate, the possibility of a chemical reaction between the metal and the ceramic, and adhesion between them [1]. These characteristics, in turn, depend on the composition of the primer coat and the temperature of its firing on metal. The traditional method for estimating the strength of adhesion of a ceramic coating to metal proposed in GOST R 51736–2001 is rather labor-consuming and requires special precision in preparing samples.

In our study we use an alternative method for fast determination of the strength of adhesion of metal to ceramic using a Micro Scratch Tester (Switzerland) and applying a scratch with the diamond indenter on a finished coating. We have estimated the strength of adhesion of a glass ceramic material intended for producing a primer (undercoat) layer of the cermet crown and a nickel-chromium alloy (62% nickel, 25% chromium; 10% molybdenum; here and elsewhere wt.%). We have tested four coatings of different compositions based on potassium-feldspar glass (Table 1) with additives of tin oxide, which is traditionally used as an opacifying agent, and hydroxyapatite, which is an alternative opacifier. For reference purposes we have tested the Duceram dental primer (Germany).

The glass composition is (%): 75 – 85 potassium feldspar, 3 – 5 B_2O_3, 3 – 5 BaO, 2 – 4 Na_2O, 2 – 4 K_2O, 5 – 7 Li_2O, and 0 – 1 ZnO. The phase composition of the finished glass ceramic materials was identified by x-ray phase analysis. The compositions of frits for primer coatings are listed in Table 1. The melting temperature of all frits was 1230°C. Furthermore, mixture 3a after melting was subjected to repeated heating at 820°C in air for its recrystallization.

All frits after melting were hardened in cold water to prevent a further growth of crystals. The frit was milled to passing through a No. 0063 sieve, then distilled water was added to prepare a suspension for its subsequent deposition on a metal substrate. The optimum firing temperature of the primer layer of the considered compositions was chosen experimentally. It is equal to 870°C (in air without exposure).

Visual inspection of the finished coatings established that coating 1 is transparent, smooth, and has vitreous luster and good adhesion to metal, but this coating does not conceal metal. Mixture 2 (potassium-feldspar glass with 10% tin oxi-

TABLE 1

Primer composition	Potassium feldspar content in glass, %	Opacifying additive		Main crystal phase of the primer
		material	content, %	
1	100	–	–	Leucite, microcline
2	90	Tin oxide	10	Leucite, orthoclase, nepheline, tin oxide
3	80	Hydroxyapatite	20	Hydroxyapatite, leucite, microcline
3a	80	The same	20	The same
“Duceram”	–	–	–	Leucite, tin oxide

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0361-7610/06/0506-0198

de) yields an opaque, white-color, slightly rough coating. Coatings 3 and 3a (potassium-feldspar glass with hydroxyapatite) are opaque, white, with a yellowish shade determined by the presence of iron impurities in the raw material. All coatings (expect composition 1) have covering properties comparable to the Duceram coating and conceal metal to a sufficient extent.

The testing of finished coatings was performed with a Micro Scratch Tester using a diamond indenter with a tip diameter of 40 μm to deposit a line. The indenter velocity was 5.248 mm/min. As the indenter was moving over the surface, we estimated the load under which the coating was torn off the metal substrate, i.e., when the indenter completely removed the upper (ceramic) layer and its pyramidal tip contacted the metal base. The moment of tearing the coating off manifested a sharp change in the curves of friction force, friction coefficient, and acoustic emission. The obtained tribometrical strength parameters of primer coats are given in Table 1.

After the scratch was applied, the coating was analyzed with a microscope. It was found that the lowest acoustic emission value (the least noise level) corresponds to the deepest penetration of the indenter into metal, i.e., the indenter moving along the more plastic component of the composite. Accordingly, an increased noise level is typical of the case where the diamond pyramid contacts the metal only with its vertex, while its edges touch the brittle nonplastic component of the composite. The noise level reflects the strength of adhesion of the coating to metal and the type of coating.

The force of friction of the indenter against the coating surface at the tear-off moment generally corresponds to the force spent on breaking off. The higher the tearing force, the higher the force of friction at the moment of tear and, consequently, the higher the strength of adhesion of the ceramic layer to metal. The maximum friction force at the breaking-off moment and, accordingly, the maximum adhesion, was registered in primer coat 3a which contains hydroxyapatite and has undergone secondary thermal treatment.

In estimating the acoustic emission, it can be assumed that the noise level generated by the indenter is related to the microstructure of the sample. Comparing the obtained average values of acoustic emission (Table 2) it can be concluded that the microstructure of coating 2 containing tin dioxide is rougher, i.e., has large crystals protruding above the surface. Therefore, the noise level generated by the indenter moving along this surface is higher than on close-crystalline surfaces 3 and 3a. Coating 1 has a smooth even surface; therefore, the noise level (acoustic emission value) is significantly lower than in coatings 2, 3, and 3a. Figure 1 shows the difference between the surface profiles of materials containing tin dioxide and hydroxyapatite. The surface profile is obtained using a Micromeasure 3D Non Contact Profilometry instrument (France).

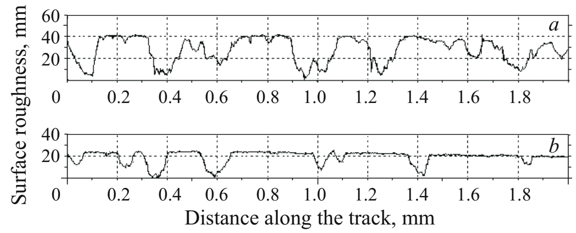

Fig. 1. Surface profile of material (composition 2) containing tin oxide (*a*) and material (composition 3) contain hydroxyapatite (*b*).

Studying the effect of the firing conditions on the properties of deposited coatings, we established that the firing temperature of 870°C, which is optimal for fixing the developed ceramic coatings 1 – 3 and 3a on metal, is insufficient for fixing the foreign coating. The Duceram coating contains a small quantity of fluxes and does not become fully vitrified at the specified temperature. This is the reason for its lower strength, compared with the other coatings bearing a higher amount of fluxes, which makes it possible to lower the firing temperature of the primer coat. Taking the example of coatings 3 and 3a, it can be noted as well that additional (stabilizing) heat treatment increases the strength of the bond of ceramics to metal due to the stable phase composition of the finished ceramic [2].

The electron microphoto (Fig. 2) shows the inhomogeneous structure of sintered primer: we can observe the intense crystallization of the target product. The relief microinhomogeneity and the porous surface are typical of primers and needed to intensify the adhesion to subsequently deposited layers.

In using traditional methods for estimating the strength of adhesion between the metal and ceramic layers, the shear method (A. A. Khoklov's method) [3] established a sufficient adhesion of the alloy to the ceramic primer coat. Its values varied from 52 to 75 MPa. In breaking tests of the strength of the bond of metal to ceramic we established the regularity of the ceramic layer breaking off the metal surface together with the oxide film. The breaking force was 24.0 – 38.2 MPa, which corroborated the high strength of bond of metal to ceramic coatings. The maximum shear and break

TABLE 2

Primer composition	Load at which coating breaks off, N	Indenter friction force, %, of maximum possible, at the moment the coating breaks off	Friction coefficient, % of maximum possible, at the moment the coating breaks off	Mean acoustic emission values, %, of maximum possible
1	0.90	13	30	30
2	0.23	5	17	65
3	0.49	12	52	46
3a	0.69	16	60	40
"Duceram"	0.03	2	5	5

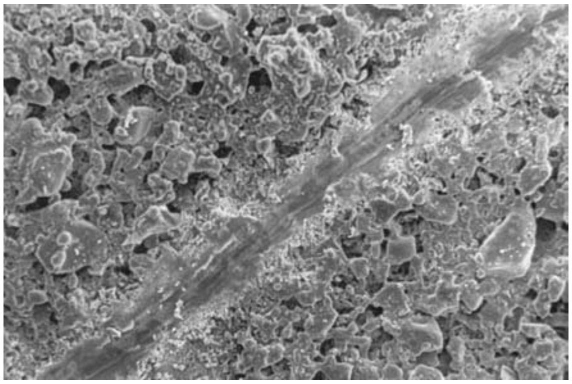

Fig. 2. Electron microscope photo of primer coat 3 with a scratch left by a diamond indenter.

forces correspond to the maximum loads at the moment of tearing off the coating. This correlates with the friction force and the friction coefficient at the break-off moment, whereas the level of acoustic emission depends on the coating relief, i.e., on the size of the protruding crystals.

It has been established that primers containing hydroxyapatite have the maximum adhesion to the substrate alloy. Additional pretreatment of frits for producing a primer increases the strength of adhesion of metal to ceramic. An additive of tin to the feldspar glass produces a rougher relief in finished coatings than a hydroxyapatite additive.

It should be noted that the Micro Scratch Tester instrument allows for the fast determination of the adhesion of the primer to the substrate alloy in a dental crown.

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